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(54) Title: METHOD FOR FRACTIONAL CRYSTALLISATION OF A MOLTEN METAL

(57) Abstract: The invention relates to a method for fractional crystallisation of an at most partially solidified molten metal. According to the invention a layer of at most partially solidified molten metal to be crystallised is cooled by a layer of cooling liquid, which is present above and/or below the layer of at most partially solidified molten metal so as to crystallise the molten metal.



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METHOD FOR FRACTIONAL CRYSTALLISATION OF A MOLTEN METAL

The invention relates to a method for fractional crystallisation of a molten metal.

Crystallisation methods and apparatus are used to refine a metal (here used as an abbreviation for metal alloy) in which too high a concentration of a foreign element is present. This foreign element can be present because in the metal made from metal ore, the primary metal, too much of the foreign element is present, or because already used metal is recycled and the foreign element concentration in the scrap is too high. For instance aluminium scrap can contain too much of the foreign elements Fe, Si or Mg for use for commercial purposes without mixing it with primary metal containing little of the foreign element.

When use is made of fractional crystallisation to refine the metal, crystals are formed in the molten metal during partial solidification of the molten metal, which crystals have a composition that is different from the composition of the molten metal that is used as a starting point.

A commercial method of fractional crystallisation for refining a metal is used in the so-called Yunnan crystalliser. This crystalliser is used for refining a tin alloy by removing Pb from Sn. The molten tin alloy is fed into an elongated container having an open top and an inclined bottom, in which container a screw is slowly rotated. The surface of the molten tin alloy is cooled by spraying water, resulting in the crystallisation of refined tin alloy. These crystals crystallise in the molten tin alloy and are transported to the shallow part of the container. Due to a temperature difference over the length of the container, in the shallow part the crystals are partially molten again, resulting in purer crystals. This mechanism repeats itself several times, and eventually very pure crystals are removed. Molten tin alloy containing Pb is removed at the deep end of the container. In this way, tin alloy containing approximately 10 % Pb can be refined into tin alloy containing approximately 0,05 % Pb.

This method for refining a metal by using the Yunnan crystalliser however cannot be used for all types of metal. One problem is that most metals have a melting point that is far higher than the melting point of the tin alloy for which the Yunnan crystalliser has been build. Because of the higher temperatures, the heat radiation is

much higher (the heat radiation increases with the fourth power of the temperature in K) and the heat losses are much higher as well. As a result of this it is much more difficult to control the temperature in the crystalliser. Another problem is that for many metals the temperature difference between the crystallisation temperature of the metal alloy and the crystallisation temperature of the pure metal is very small, in the order of a few K. The Yunnan crystalliser cannot be used for such small differences in crystallisation temperature. A secondary problem is that the use of a screw poses problems in some metals, because the metals normally used for the screw dissolve in these molten metals. A general problem is that the crystals formed in the molten metal tend to adhere to the walls of the crystalliser or the screw.

It is an object of the invention to provide an improved method particularly suitable for fractional crystallisation and refinement of aluminium and suchlike metals having a high melting point.

It is another object of the invention to provide a method with which the temperature of the molten metal with the crystals can be controlled accurately.

It is still another object of the invention to provide a method with which the crystals will be in suspension in the molten metal, without attachment to a screw.

It is a further object of the invention to provide an improved method for the continuous fractional crystallisation of metals.

One or more of these objects are reached with a method for fractional crystallisation of an at most partially solidified molten metal, in which a layer of at most partially solidified molten metal to be crystallised is cooled by a layer of cooling liquid which is present above and/or below the layer of at most partially solidified molten metal so as to crystallise the molten metal.

The use of a cooling liquid to cool the molten metal so as to produce refined crystals is advantageous for a number of reasons. Firstly, the cooling liquid can take up a lot of energy so the energy that has to be dissipated due to the crystallisation can be easily removed. The temperature of the cooling liquid can be measured and controlled to control the temperature of the molten metal, whereas a mere cooling through the walls of a crystallisation apparatus can not be used to accurately control the temperature of the molten metal. If the cooling should not only be effected through the walls of the apparatus, it normally has to be supplemented by way of a

cooling device using a cooling coil or such an arrangement, which will cool the molten metal only at one exact place and on which the molten metal could crystallise, hampering the cooling effect of the cooling device.

Secondly, a cooling liquid will either be heavier or lighter than the molten metal, so the molten metal will float on the heavier cooling liquid or the lighter cooling liquid will float on the molten metal, or both if two types of cooling liquid are used. Crystals formed in molten metal will either sink through the molten metal or rise in the molten metal, and will end against a wall or against a cooling layer. This means that the crystals remain in suspension in the molten metal. It would be possible to separate the layer of cooling liquid and the layer of molten metal by a thin partition wall which does not hamper the cooling by the cooling liquid very much and to which the crystals do not adhere.

Preferably the layer of cooling liquid is only present below the layer of at most partially solidified molten metal. This is preferable because for most commercially interesting metals the crystals sink in the molten metal.

In a preferred embodiment the layer of cooling liquid contacts the layer of at most partially solidified molten metal. In this way no partition wall is present which would hamper the cooling effect of the cooling liquid and to which the crystals could adhere.

Preferably the layer of cooling liquid is cooled at at least one spot near the layer of at most partially solidified molten metal. To do so, the cooling liquid can be cooled using one or more cooling devices placed at desired spots in a crystallisation apparatus used for implementing the method. Because the cooling liquid is cooled and not the molten metal, it is possible to accurately cool the molten metal such that crystals are formed in the molten metal near the place where the cooling device is present in the cooling liquid. The energy that has to be dissipated because of the crystallisation of molten metal is thus removed at the desired spot.

According to a preferred embodiment of the method the cooling liquid is transported relative to the layer of at most partially solidified molten metal. The transportation of the cooling liquid relative to the layer of molten metal and, in practice, relative to a crystallisation apparatus used for implementing the method, means that part of the cooling liquid is removed from the apparatus and new cooling

liquid is introduced into the apparatus. Thus, dissipated energy is removed from the layer of cooling liquid that is present above an/or below the molten metal. In this way a very effective and very accurate way of cooling the molten metal is used, since the transportation velocity of the cooling liquid can be used to accurately remove energy from the molten metal. The transportation of the cooling liquid relative to the layer of molten metal also means that a temperature difference will exist over the length of the layer of cooling liquid, since the cooling liquid takes up energy from the molten metal during its transportation, so the cooling liquid will have a lower temperature where it is introduced and a higher temperature where it is removed. As a result also the layer of molten metal will possess a temperature gradient over its length, being slightly colder where the cooling liquid has a lower temperature and being slightly warmer where the cooling liquid has a higher temperature. The consequence is that crystals will be first formed in the coolest part of the layer of molten metal. These crystals will rise or sink to the layer of cooling liquid and once they are near or against the cooling layer they are transported together with the cooling layer. Due to the temperature gradient in the molten metal, the crystals are transported to a warmer part of the layer of molten metal. Here the crystals formed in the cooler part of the layer of molten metal recrystallise and thereby become more (or less) refined. This mechanism repeats itself through the length of the layer of molten metal. In this way very refined crystals are formed (or very refined molten metal is left) at the end of the layer of molten metal, depending on the length of the layer of molten metal. The crystals and/or molten metal can be removed near the place where the cooling liquid is removed.

Preferably, the cooling liquid is recycled and more preferably cooled. The cooling liquid is regenerated in this way, and by cooling it the temperature at which it is introduced into the layer of cooling liquid can be controlled. Together with the recycling velocity in this way the cooling capacity is given, if no separate cooling devices are used. Moreover, in the layer of cooling liquid a temperature gradient will exist between the spot where the cooled cooling liquid is introduced into the layer and the spot where the cooling liquid is removed from the layer.

According to a particularly preferred embodiment the molten metal is transported relative to the layer of cooling liquid. In this way it is possible to

introduce fresh molten metal in a crystallisation apparatus for implementing the method, by which a continuous fractional crystallisation of the molten metal can be realised.

Of course it is preferred if both the cooling liquid and the molten metal are
5 both transported relative to the crystallisation apparatus, such that a continuous crystallisation with an accurate cooling is possible.

Preferably the cooling liquid that is used is a molten salt. A molten salt will not easily react with the molten metal or with metal crystals, and has a high cooling capacity.

10 According to a preferred embodiment the layer of at most partially solidified molten metal is divided into compartments that communicate near the layer of cooling liquid. Each of the compartments in this way in principle forms its own crystallisation apparatus, but the crystals that are formed in one compartment and are risen or sunk to the layer of cooling liquid are transported to the next compartment, if
15 the cooling liquid is transported in a crystallisation apparatus used for implementing the method. Due to the cooling of the cooling liquid crystals are formed in the molten metal. The selective transport of crystals results in a gradient in the metal purity over the length of the layer of molten metal, resulting in a temperature gradient in the layer of molten metal. The temperature in each compartment therefore slightly differs
20 from the temperature in the next compartment, and crystals formed in one compartment can partially melt again in the next compartment to which they are transported by the cooling liquid, because in that compartment the temperature is higher. In this way a cascade of crystallisation apparatus is formed, by which the crystals formed at the high temperature end of the layer of cooling liquid will have a
25 high or low purity as compared to the molten metal.

Preferably, the at most partially solidified molten metal is stirred. By stirring the partially molten metal the crystals are kept in suspension and will not all rise or sink to the layer of cooling liquid.

In case the layer of at most partially solidified molten metal is divided into
30 compartments, preferably the at most partially solidified molten metal is stirred in at least one compartment, more preferably in all compartments. As a result in each

compartment in which the molten metal is stirred suspension crystallisation takes place.

According to a preferred embodiment of the method at most partially solidified molten metal is added between both ends of the length of the layer of at most partially solidified molten metal, and refined metal is removed at one end and remaining molten metal is removed at the other end of the layer of metal. By introducing the at most partially solidified molten metal in which fractional crystallisation still has to take place between both ends of the length of the layer of at most partially solidified molten metal, at one end the refined metal can be removed and the remaining molten metal can be removed at the other end.

Preferably, the metal used is aluminium. Aluminium is one of the metals for which the above method for fractional crystallisation is particularly suited.

The fractional crystallisation as described above is preferably used for removing Cu, Fe, Ga, Mg, Mn, B, Si, Sn, Zn or Ni from aluminium.

The invention will be elucidated referring to an exemplary embodiment, in view of the accompanying drawing.

Fig. 1 shows, in a schematic way, a cross section through a crystallisation apparatus for implementing the method according to the invention.

Fig. 1 shows a crystallisation apparatus 1 for the continuous fractional crystallisation of a molten metal containing one or more foreign elements. The crystallisation apparatus 1 has a chamber 2 with a wall 3, which wall is very well isolated as is known in the art, normally by special refractory materials.

In the chamber 2 of the apparatus is present a layer of cooling liquid 4, for instance molten salt, and a layer of partially molten metal 5, for instance aluminium with crystals. The cooling liquid can be drawn into (see arrow A) and transported through a recirculation pipe 6 by means of a pump 7. A cooling device 8 is present in the pipe 6 to cool the cooling liquid before it re-enters the chamber 2 (see arrow B).

The layer of partially molten metal 5 is present on the layer of cooling liquid 4, floating on the layer of cooling liquid 4. In the layer of molten metal 5 crystals are formed due to the cooling of the cooling liquid 4. Molten metal without crystals is supplied through an inlet 10 (arrow D). Molten metal with crystals is discharged through an outlet 11 (arrow E) at one end of the chamber 2, and molten metal

containing a lot of the foreign element as a by-product is discharged through an outlet 12 (arrow F). The outlet 12 is present at the end of the chamber where the cooling liquid re-enters the chamber 2, and the outlet 11 at the other end of chamber 2. The inlet 10 can be present anywhere between the outlets 11 and 12, but is
5 preferably present somewhere halfway the two ends of chamber 2.

In chamber 2 a number of compartments are formed by placing compartment walls 13 transverse in chamber 2. These compartment walls extend from the walls of chamber 2, both in the layer of cooling liquid and in the layer of partially molten metal, but end at a certain distance from the contact surface 14 between the layers.
10 The number of compartments formed by the compartment walls can be varied depending on the type of metal, the contamination of the metal to be refined and the desired degree of refinement.

In each compartment formed in the layer of cooling liquid a cooling element 15 can be present for additional cooling of the cooling liquid. In each compartment in
15 the partially molten metal a mixing element 16 can be present for stirring the molten metal with crystals, to keep the crystals in suspension and to enhance the exchange of material in the crystals and the molten metal.

The above described crystallisation apparatus can for instance be used for the continuous fractional crystallisation of aluminium containing 0.10% Si and 0.20% Fe
20 (so-called P1020) to reach aluminium containing less than 0.01% Si and 0.01% Fe (so-called P0101).

For this crystallisation process chamber 2 of the crystallisation apparatus 1 has to have fifteen compartments in each layer, each compartment for the molten aluminium having a size of approximately $500 \times 500 \times 500 \text{ mm}^3$ and each compartment
25 for the cooling liquid having a size of approximately $500 \times 500 \times 300 \text{ mm}^3$, so the chamber has an inner size of approximately 7.5 m (length) x 0.5 m (width) x 0.8 m (height).

The cooling liquid has to be heavier than the molten aluminium at approximately 660°C , which has a density of 2400 kg/m^3 . The cooling liquid can be
30 a salt of NaCl and KCl and/or NaF and KF containing BaCl_2 and BaF_2 . With this composition a density of 3000 kg/m^3 and a melting point of 500°C can be reached.

The method according to the invention implemented for aluminium with the above-described apparatus is as follows.

Molten aluminium with P1020 composition is introduced through inlet 10 at a temperature just above the crystallisation temperature of approximately 660° C. At the contact surface 14 the layer of molten aluminium 5 contacts the layer of molten salt 4, and since the temperature of the molten salt is kept lower than the temperature of the molten aluminium, the temperature of the molten aluminium decreases and crystals are formed. These crystals contain less of the foreign elements Si and Fe and slowly sink through the molten aluminium onto the layer of molten salt.

The molten salt is transported through chamber 2 of the crystallisation apparatus 1 during which it takes up energy from the molten aluminium, before it enters the recirculation pipe 6 due to the pumping of pump 7, and is cooled in the cooling device 8. The cooled molten salt re-enters the chamber 2 to cool the molten aluminium again. The molten salt is transported with a velocity of 1 to 3 m³ per hour. On its way through the chamber 2, the molten salt takes with it the crystals that have sunk onto the layer of molten salt. The transportation of the molten salt through the chamber also results in the transportation of part of the molten aluminium, generally indicated by the arrows G. However, not all of the molten aluminium with crystals that is transported is discharged through outlet 11, so there is also a counter current generally indicated by the arrows H.

Due to the energy the molten salt takes up from the molten aluminium, the layer of molten salt 4 is gradually heated up from the left end to the right end of the chamber as seen in Fig. 1. As a result thereof, there is also a temperature difference in the molten aluminium, the molten aluminium having a lower temperature at the left end and a higher temperature at the right end of the chamber as seen in Fig. 1.

This temperature gradient in the molten aluminium is very useful for the continuous fractional crystallisation according to the invention. A crystal that is formed in one compartment of the chamber is formed at a certain temperature of the molten aluminium; it will be more refined than the molten aluminium in which it is formed. When this crystal has sunk towards the molten salt and has been transported to the next compartment, it will be present in a compartment wherein the temperature of the aluminium is somewhat higher. The result will be that that crystal will partly

or totally melt, which leads to a composition of the molten aluminium in that compartment that is more refined than the molten aluminium in the compartment to the left of it. In this compartment crystals will be formed again, which will also be more refined than the molten aluminium they are formed in. Crystals that are formed
5 in a right-hand compartment will therefore be more refined than the crystals formed in an adjacent left-hand compartment.

This mechanism occurs in all compartments of the chamber, resulting in highly refined crystals at the right-hand end of the chamber and by-product with a high concentration of Si and Fe at the left-hand end of the chamber.

10 The mixing elements 16 are used to stir the molten aluminium in each compartment such that not all the crystals formed sink to the layer of molten salt, and in each department a new equilibrium can be reached between the composition of the molten aluminium present in that compartment and the crystals formed therein. The size and rotational speed of the mixing elements depend on the size of the
15 crystals to be formed and the velocity of the molten salt.

For the control of the crystallisation, the apparatus is preferably equipped with means to measure and control the solid fraction, the chemical composition and/or the temperature in the layer of metal.

With the above-described apparatus, a production of about 20 tons per day of
20 aluminium with P0101 composition can be reached; the by-product will be only some 10 % thereof.

It will be understood that many changes can be made or will be necessary depending on the metal used and the foreign element that has to be removed from it. Moreover, it will not always be necessary to include all the components of the
25 crystallisation apparatus 1 as shown in Fig. 1. For instance, one or more or even all cooling elements 15 could be left out, and/or the or some of the compartment walls 13 in the molten salt could be left out, and/or one or more mixing elements 13 could be left out, and even the recirculation pipe 6 with pump 7 and cooling device 8 could be left out if there is no need to transport the molten metal and the apparatus is used
30 for a batch process. It will be clear that these changes in the apparatus will influence the method for the fractional crystallisation of a molten metal. Thus, the scope of the invention will only be determined by the accompanying claims.

CLAIMS

1. Method for fractional crystallisation of an at most partially solidified molten metal, characterised in that a layer of at most partially solidified molten metal
5 to be crystallised is cooled by a layer of cooling liquid which is present above and/or below the layer of at most partially solidified molten metal so as to crystallise the molten metal.
2. Method according to claim 1, in which the layer of cooling liquid is only
10 present below the layer of at most partially solidified molten metal.
3. Method according to claim 1 or 2, in which the layer of cooling liquid contacts the layer of at most partially solidified molten metal.
- 15 4. Method according to claim 1, 2 or 3, in which the layer of cooling liquid is cooled at at least one spot near the layer of at most partially solidified molten metal.
5. Method according to any one of the preceding claims, in which the cooling
20 liquid is transported relative to the layer of at most partially solidified molten metal.
6. Method according to claim 5, in which the cooling liquid is recycled and preferably cooled.
25
7. Method according to any one of the preceding claims, in which the molten metal is transported relative to the layer of cooling liquid.
8. Method according to any one of the preceding claims, in which the cooling
30 liquid that is used is a molten salt.

9. Method according to any one of the preceding claims, in which the layer of at most partially solidified molten metal is divided into compartments that communicate near the layer of cooling liquid.
- 5 10. Method according to any one of the preceding claims, in which the at most partially solidified molten metal is stirred.
11. Method according to claim 10 in combination with claim 9, in which the at most partially solidified molten metal is stirred in at least one compartment,
10 preferably in all compartments.
12. Method according to any one of the preceding claims, in which at most partially solidified molten metal is added between both ends of the length of the layer of at most partially solidified molten metal, and refined metal is
15 removed at one end and remaining molten metal is removed at the other end of the layer of metal.
13. Method according to any one of the preceding claims, in which the metal used is aluminium.
20
14. Method according any one of the preceding claims for removing Cu, Fe, Ga, Mg, Mn, B, Si, Sn, Zn or Ni from aluminium.

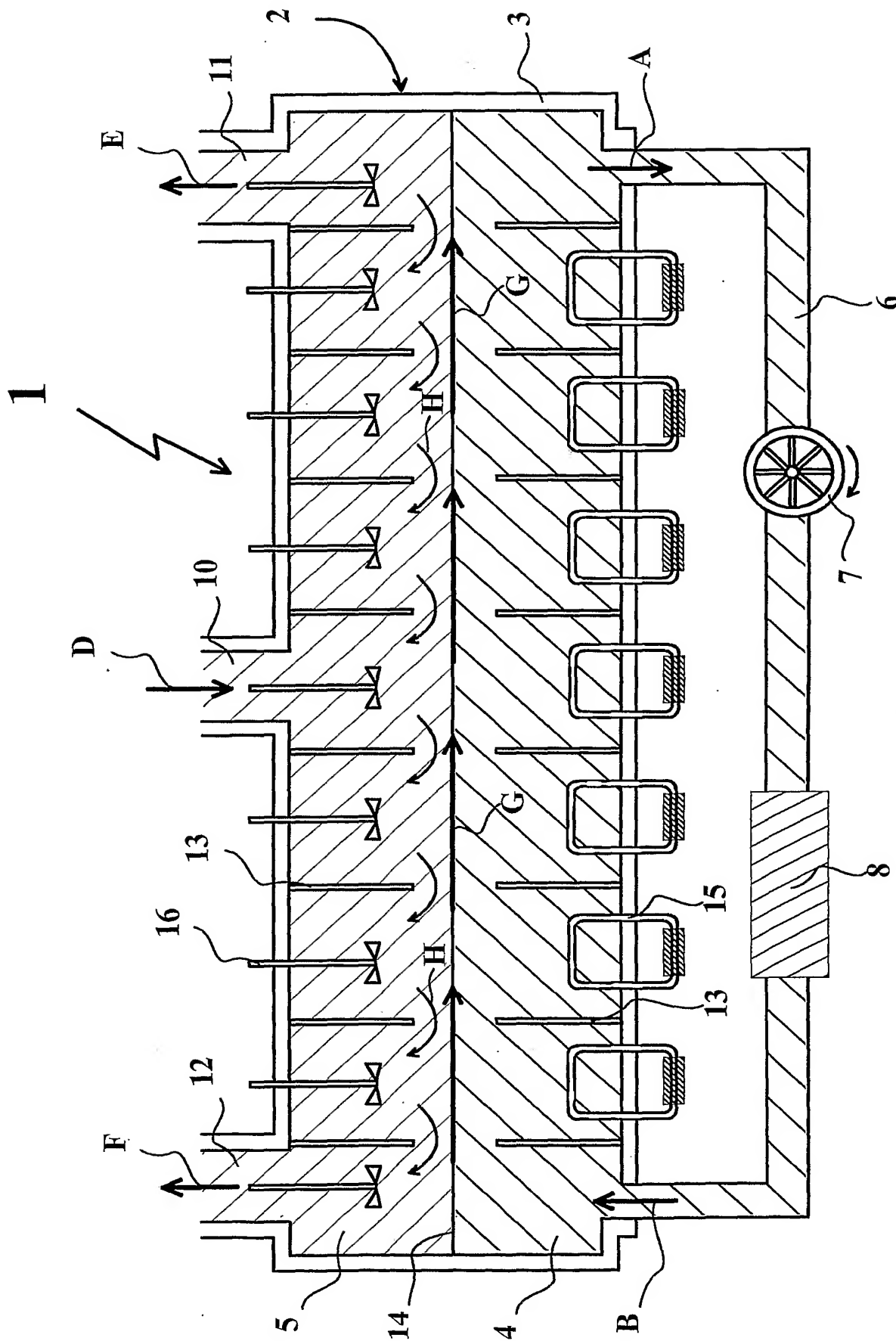


Fig. 1

INTERNATIONAL SEARCH REPORT

International Application No.

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A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C22B21/06

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C22B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, PAJ, WPI Data, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	PATENT ABSTRACTS OF JAPAN vol. 007, no. 205 (C-185), 9 September 1983 (1983-09-09) -& JP 58 104132 A (MITSUBISHI KEIKINZOKU KOGYO KK), 21 June 1983 (1983-06-21) abstract; figures ---	1,2,4-14
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Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

* Special categories of cited documents :

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INTERNATIONAL SEARCH REPORT

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

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